UDC 666.295:546.723

PRODUCTION OF IRON-CONTAINING CRYSTALLINE GLAZES

I. N. Dvornichenko[1] and S. V. Matsenko[1]

Translated from Steklo i Keramika, No. 2, pp. 28 – 29, February, 2000.

Results of production of crystalline glaze with a decorative aventurine effect are given. Synthesis of glaze was performed based on frit containing Na_2O, B_2O_3, and SiO_2 using the simplex-lattice method of experiment design. It is established that the aventurine effect is caused by hematite crystals.

Glaze coatings with an aventurine effect are used in the production of household and decorative ceramics to make the products more expressive, more water-resistant, more waterproof, etc. The aventurine effect is currently understood as color glazes and glasses that develop a scintillation effect on the background of the glass matrix. In iron-containing glasses and glazes this effect is caused by crystals of hematite and fayalite (USSR Inv. Certif. No. 601244).

In studying the special features of low-melting iron-containing aluminoboron silicate glazes, researchers from Riga [1] established the possibility of producing crystalline glaze in which hematite crystals are distinguished on the dark brown background of the glass matrix. In this case crystallization is manifested when the Fe_2O_3 content is over 15% (here and elsewhere weight content is indicated).

The synthesis of aventurine glazes and glasses has its own special features consisting in the mechanism of aventurine formation. It is known that separation of a crystalline phase from a glass melt is caused by oversaturation of the mel twith some component. In our case this is Fe^{3+} cations in the octahedral coordination. Similarly to Al^{3+} cations, six-coordination iron cations are dissolved in a glass melt at high temperatures, and as the melt is cooled, they are capable of crystallizing [2].

The present work is devoted to the problems of obtaining crystalline glazes with an aventurine effect and studying their properties.

Using the simplex-lattice method of experiment design [3] glaze mixtures were prepared based on A-1 frit containing Na_2O, B_2O_3, SiO_2. The frit was melted in a silite furnace at a temperature of 1375 ± 25°C for 45 – 60 min, and then it was poured into water. The crystallizing ability of the frit was studied in a gradient furnace in the temperature interval of 500 – 900°C. The glass frit does not become crystallized after heat treatment for 1 h in the indicated temperature interval.

[1] Ukrainian State Chemical Engineering University, Dnepropetrovsk, Ukraine.

Glaze slips were prepared by wet grinding of the frit, ferric oxide, and clay until they passed through a sieve with 10,000 cells/cm². The finished slips were aged for at least 24 h before deposition. The glaze suspension was deposited on the crock by casting. The glazed articles were subjected to accelerated firing with a total cycle of heating, firing, and cooling lasting 7 – 8 h. The admissible temperature interval for glaze firing (900 – 1100°C) and the optimum temperature for their deposition (980 – 1050°C) were found by firing glazed articles at different temperatures.

As a result of visual observation of the glaze coating it was found that crystals of iron compounds become visible at an Fe_2O_3 content over 20% and a clay content over 5% for glazes based on A-1 frit. Thus, for the synthesis of crystalline glazes, a simplex was chosen (Fig. 1) having at its vertices compositions 6, 16, and 18, which are characterized by an Fe_2O_3 content of 20 – 25%.

The TCLE, the initial softening temperature, and water resistance for the selected glaze compositions were determined by standard methods (Fig. 2).

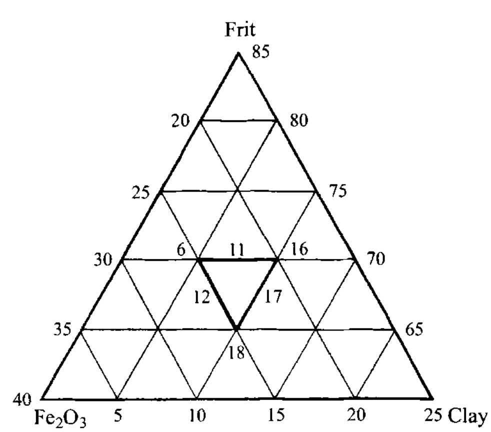

Fig. 1. Position of the experiment design simplex on the ternary diagram

0361-7610/00/0102-0067$25.00 © 2000 Kluwer Academic/Plenum Publishers

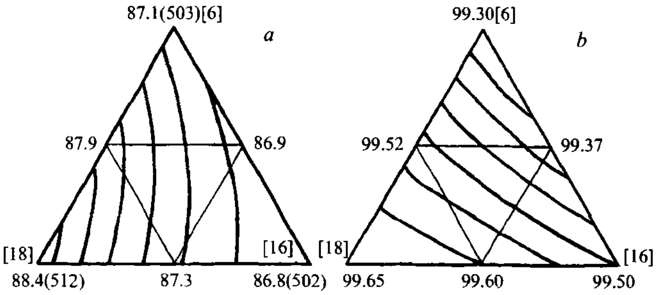

Fig. 2. Physicochemical properties of glazes (compositions are indicated in square brackets): *a*) TCLE (10^{-7} °C^{-1}); the temperature of initial softening is indicated in parentheses (°C); *b*) water resistance (weight retention after boiling in water for 1 h, %).

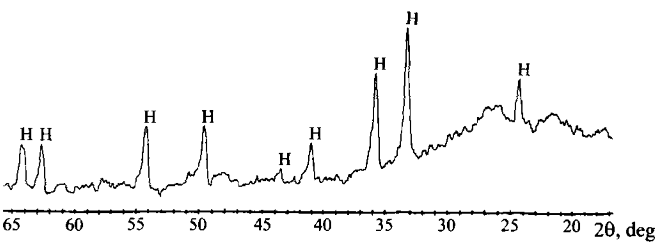

Fig. 3. Typical x-ray pattern of glazes containing 25% Fe_2O_3.

According to the data obtained, it is possible to use a glaze with 20 – 25% Fe_2O_3 and 5 – 10% clay to synthesize a coating with a decorative aventurine scintillation effect and good physicochemical parameters. Glaze 18 with 25% Fe_2O_3 and 10% clay, as a result of which finely disperse crystallization takes place, is the best with respect to water resistance.

Using x-ray phase analysis, it was found that glazes exhibiting a scintillation effect contain hematite (α-Fe_2O_3) crystals in the vitreous phase, and the effect is caused by these crystals. A typical x-ray pattern of glazes containing 25% Fe_2O_3 is shown in Fig. 3.

In studying the mechanism of aventurine formation and refining the firing conditions for glaze composition 6, a temperature dependence of crystal growth was revealed. The optimum quantity and size of the crystals causing a scintillation effect were observed at a heat-treatment temperature of 900 ± 5°C. With the temperature decreased to 880°C and below, surface crystallization was manifested in addition to volume crystallization in the glaze layer, which degraded the exterior of the glaze.

Based on the glaze coating of composition 6, the relationship between the aventurine effect and the glaze-layer thickness was investigated. It was found that the aventurine effect was manifested to a maximum extent in a thin (0.1 – 1.5 mm) glaze coating. As the glaze-coating thickness was increased to 2 mm, manifestation of red scintillation of hematite crystals inside the glass matrix appeared. Due to the dark color of the glass matrix, not all hematite crystals in the glaze volume and especially on the inner surface of the glaze could be visually observed. For maximum display of the aventurine effect, it is recommended that the glaze slip be deposited on the ceramic substrate so that the coating thickness after firing is 0.2 – 1.6 mm.

Thus, crystalline glazes with a decorative aventurine effect were obtained based on frit of the Na_2O – B_2O_3 – SiO_2 system. Since such glazes have a rather high TCLE and a low firing temperature, it is recommended that they be used in production of majolica ware. In the case of a specific ceramic material with known physicochemical parameters, it is possible, by composition optimization, to change the TCLE and the firing temperature of these glazes, which will make it possible to extend their application to faience and porcelain products.

REFERENCES

1. I. F. Dzalb, A. P. Raman, and Yu. A. Mikelsons, "The effect of iron compounds on the structure and properties of aluminoboron silicate glazes," in: *Inorganic Glasses, Coatings, and Materials* [in Russian], Riga (1985), pp. 89 – 94.
2. Ya. A. Fedorovskii, "The effect of some oxides on the crystallization properties of glass," in: *Catalyzed Crystallization of Glass* [in Russian], Moscow (1982), pp. 41 – 45.
3. I. G. Zedgenidze, *Planning of Experiments to Study Multicomponent Systems* [in Russian], Nauka, Moscow (1976).